An Approach to Calculate Thermodynamic Properties of Mixtures Including Propane, n-Butane and Iso-Butane[1]

J. Avsec[2,4], K. Watanabe[3], M. Marčič[2]

[2]University of Maribor, Faculty of Mechanical Engineering, Smetanova 17, 2000 Maribor, SLOVENIA

[3]Keio University, Department of System Design Engineering, Faculty of Science and Technology, Yokohama 223-8522, JAPAN

[4]To whom corresspondence should be addresseed. Email: jurij.avsec@uni-mb.si

Abstract

This paper discusses the mathematical model for computing the thermodynamic properties of propane, n-butane and iso-butane and their mixtures, in its fluid phase with an aid of statistical chain theory. The constants necessary for the computation like the characteristic temperatures of rotation, electronic state etc. and the moments of inertia are analytically obtained applying the knowledge of the atomic structure of the molecule. In the paper is presented the procedure for calculating essential thermodynamic properties such as pressure, speed of sound, the Joule-Thomson coefficient, compressibility, enthalpy and thermal expansion coefficient. This paper will discuss, for the first time, the application of statistical chain theory and accuracy for binary and ternary mixtures including propane, n-butane and iso-butane, in their entire fluid phases for all the important thermodynamic properties. To calculate the thermodynamic properties of Lennard-Jones chains,we have used the Kolafa-Nezbeda and Johnson-Zollweg-Gubbins models. The thermodynamic properties of the Lennard-Jones mixtures are obtained using the one-fluid theory.

Keywords: hydrocarbon, mixtures, refrigerant, statistical thermodynamics, thermodynamic properties.

1. INTRODUCTION

In the engineering practice energy-conversion systems, operating in liquid-gas region are of vital importance. In order to design devices of this field of activity, it is necessary to know the thermodynamic properties of state in a one and two phase environment for pure hydrocarbons and their mixtures.

In most cases the thermodynamic tables or diagrams or different empirical functions obtained from measurement are used (classical thermodynamics). Today, there are numerous equations of state (EOS) reported in the literature for describing the behaviours of fluids: (Van der Waals EOS (VDW), Peng-Robinson (PR), Redlich-Kwong (RK) EOS, Soave EOS..) [1]. However, these equations have exhibited some noticeable defects, such as poor agreement with experimental data at moderate densities. On the other hand, we can use the complex equations of state with many constants (Benedict-Webb-Rubin [1] (BWR) EOS, Lee-Kessler[1] EOS, Benedict-Webb-Rubin-Starling-Nishiumi [1] EOS, modified BWR [1,2] (MBWR), Jacobsen-Stewart [2,3] EOS (JS), Tillner-Roth-Watanabe-Wagner [4-9] (TRWW)…). These equations are more complicated but they have no insight into the microstructure of matter and poor agreement with experimental data outside interpolation limits.

Statistical thermodynamics [10-24], on the other hand, calculates the properties of the state on the basis of molecular motions in a space and intramolecular interaction. The calculation of the thermodynamic functions of state is possible by many statistical theories. One of the most successful approaches is the perturbation theory. Several equations of state have been published that are based on perturbation theory [10,11]. The evolution of perturbation theory is well described by Barker and Henderson [10,12], Münster [13], Lucas [14] and Gray & Gubbins [15]. In recent years

thermodynamic theories based on statistical thermodynamics have been rapidly developed. Fluids with chain bonding and association have received much attention in recent years. Interests for these fluids are accelerated by the fact that they cover much wider range of real fluids than spherical ones [25]. In reference [21] is explained in detail the advantage of SAFT models in comparison with classical statistical mdels over the entire fluid region.

In these paper we developed the mathematical model of computing the equilibrium properties of state on the basis of statistical chain theory. All these models are based on Lennard-Jones intermolecular potential function. The Lennard-Jones intermolecular potential is an important model for studying of simple fluids in one- and two-phase region. It is widely used as a reference potential in perturbation theories for more complex potentials [15,16].

We compared the deviation of the results between various models for thermodynamic functions of state and also for their derivatives (enthalpy, pressure, entropy, isothermal compressibility, coefficient of thermal expansion, heat capacities, speed of sound) too.

The results of the analysis are compared with the TRWW model obtained on the basis of classical thermodynamics and show a relatively good agreement, especially for real gases. Somewhat larger deviations can, however, be found in the region of real liquid due to the large influence of the attraction and repulsion forces, since the Lennard- Jones potential is an approximation of the actual real intermolecular potential.

2. STATISTICAL ASSOCIATING FLUID THEORY (SAFT) [25-51]

Over the last fifthy years, quite accurate models on the basis of statistical thermodynamics have been developed for predicting the thermodynamic properties for simple molecules. By simple we mean molecules for which the most important intermolecular forces are repulsion and dispersion with weak electrostatic forces due to dipoles, quadrupoles and higher multipole moments. Many hydrocarbons, natural constituents, simple organic and simple inorganic molecules fall within this category. But a lot of other components such as electrolytes, polar solvents, hydrogen-bonded fluids, polymers, liquid crystals, plasmas and particularly mixtures do not belong to this group. The reason for this is that, for such fluids, new intermolecular forces become important: Coloumbic forces, strong polar forces, complexing forces, the effects of association and chain formation...

An important sort of these complex fluids consists of those that associate to form relatively long-lived dimmers or higher n-mers. This sort of fluids includes hydrogen bonding, where the charge transfer of other types can occur. The intermolecular forces involved are stronger than those due to dispersion or weak electrostatic interactions but still weaker than forces due to chemical bonds.

A good theory for these fluids will be very beneficial to chemical engineering applications by reducing the number of parameters and making them more physically meaningful and more predictable. In technical practice energy conversion sytems are of vital importance. To calculate the thermodynamic properties of real Lennard-Jones (LJ) fluid, **Liu-Li-Lu (LLL)** (revisited Cotterman) equation of state based on simple perturbation theory and SAFT-VR equation of state for LJ chain fluid was applied. The developed RDF has been applied to the development of a new SAFT model. The

present model has been used to calculate several typical properties of LJ chains and associating LJ chains. This paper for the first time discusses the accuracy of the present models in real engineering practice.

The original derivation of SAFT models can be shown by Wertheim papers [41-44]. They require a comprehensive knowledge of graph theory to be fully understood. With a help of SAFT theory we can express the residual part of free energy as:

$$A^{res} = A^{seg} + A^{chain} + A^{assoc} \quad (1)$$

For the pure components we can express more detailed equation:

$$A^{res} = A^{seg}(m\rho, T, \sigma_s, \varepsilon) + A^{chain}(\rho, d, m) + A^{assoc}(\rho, T, d, \varepsilon^{AB}, \kappa^{AB}) \quad (2)$$

where ρ is the molar density of molecules, m is number of segments, ε^{AB} is association energy of interaction between two sites and κ^{AB} is volume interaction between two sites.

The residual Helmholtz energy consists of three terms representing contribution from different intermolecular forces. The first term A^{seg} represents segment-segment interactions. In the present paper are segment-segment interactions represented through Lennard-Jones interaction potential. Each segment is characterized by its diameter σ_s, segment interaction parameter ε_s, and each molecule is characterized with the number of segments, m.

The second term A^{chain} is the result of presence of covalent chain-forming bonds between the LJ segments.

The third term A^{assoc} is the result of site-site interactions between segments, for example we can mention hydrogen bonding. For the hydrocarbons the association term is of no importance and will be neglected in our equations.

3. Liu-Li-Lu model [26]

The present model is developed on the basis of SAFT and perturbation theory around hard sphere with new coefficients by fitting reduced pressure and internal energy data from molecular simulation:

$$A^{seg} = A^{hs} + A^{pert} \tag{3}$$

The hard sphere term A^{hs} is calculated with the expression given by Mansoori et al. [51]:

$$\frac{A^{hs}}{R_m T} = \frac{6}{\pi\rho}\left[\frac{3\xi_1\xi_2}{1-\xi_3} + \frac{{\xi_2}^3}{{\xi_3}^2(1-\xi_3)^2} + \left(\frac{{\xi_2}^3}{{\xi_3}^2} - \xi_0\right)\ln(1-\xi_3)\right] \tag{4}$$

where the symbol ξ_i is expressed as:

$$\xi_i = \left(\frac{\pi}{6}\right)\rho\sum_i \psi_i m_i {d_i}^i \tag{5}$$

In Eq. (5) d_i represents the hard sphere diameter and is temperature dependent function ans ψ_i is molar fraction of component i. In our case we have used the equation developed by Cotterman et al. [52]:

$$d_i = \sigma_i \frac{1 + 0.2977T^*}{1 + 0.33163T^* + c_3 T^{*2}} \tag{6}$$

where T^* is reduced temperature

$$c_3 = \left(0.0010477 + 0.025337\frac{m_i - 1}{m_i}\right) \tag{7}$$

In the case of pure fluid Eq. (4) is reduced into Carnahan-Starling equation [12]:

$$\frac{A^{hs}}{R_m T} = m\frac{4\eta - 3\eta^2}{(1-\eta)^2}, \tag{8}$$

For the dispersion therm we have used Cotterman et al [52]. equation and one dimensional VDW theory for mixtures [26]:

$$A^{pert} = m_x \frac{A^{(1)}}{T_x^*} + m_x \frac{A^{(2)}}{T_x^{*2}} \tag{9}$$

$$\frac{A^{(1)}}{R_m T} = \sum_{m=1}^{4} A_{1m} \left(\frac{\eta}{\tau}\right)^m, \quad \frac{A^{(2)}}{R_m T} = \sum_{m=1}^{4} A_{2m} \left(\frac{\eta}{\tau}\right)^m, \tag{10}$$

$$\tau = 0.7405, \qquad \eta = \frac{\pi \rho d_s^{\,3}}{6} m_x, \tag{11}$$

The effective segment diameter d_s is determined on the basis of Barker perurbation theory. We use a function developed in the work of Chapman et al [27].

$$d_s = \sigma_x \frac{1 + 0.2977 T^*}{1 + 0.33163 T^* + c_3 T^{*2}} \tag{12}$$

$$c_3 = 0.0010477 + 0.025337 \frac{m_x - 1}{m_x} \tag{13}$$

where

$$T_x^{\,*} = \frac{kT}{\varepsilon_x} \tag{14}$$

For the mixtures we have used VDW1 mixing rules [17,18]:

$$\begin{aligned} m_x &= \sum_i \psi_i m_i \\ m_x^{\,2} \sigma_x^{\,3} &= \sum_i \sum_j \psi_i \psi_j m_i m_j \sigma_{ij} \\ m_x^{\,2} \varepsilon_x \sigma_x^{\,3} &= \sum_i \sum_j \psi_i \psi_j m_i m_j \varepsilon_{ij} \sigma_{ij} \end{aligned} \tag{15}$$

For the determination of mixing parameters we have used Lorentz-Berthelot equation:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \tag{16}$$

According to Wertheim first order thermodynamic perturbation theory, the contribution to free energy due to chain formation of the LJ system is expressed as:

$$\frac{A^{chain}}{NkT} = \sum_i \psi_i (1 - m_i) \ln g^{LJ}(\sigma) \tag{17}$$

Johnson et al. [29] gave a correlation result of the radial distribution function for LJ fluids dependent on reduced temperature and reduced density:

$$g^{LJ}(\sigma_s) = 1 + \sum_{i=1}^{5} \sum_{j=1}^{5} a_{ij} (\rho^*)^i (T^*)^{1-j} \tag{18}$$

4. RESULTS AND COMPARISON WITH EXPERIMENTAL DATA

The constants necessary for the computation such as the characteristic rotation-, electronic etc. temperatures are obtained from data [53-56]. The vibration constants are obtained in NIST Chemistry Web Book page. The moments of inertia are obtained analytically by applying the knowledge of the atomic structure of the molecule. We carried out calculations for mixtures of n-butane and iso-butane (C_4H_{10}) and propane (C_3H_8). The comparison of our calculations for HC mixtures with TRWW model, is presented in Figures 1-4. They show the relative deviation of the results for mixtures between butane and propane in the real gas region between the analytical computation (Liu-Li-Lu model (LLL)), and TRWW model obtained by classical thermodynamics. For the purpose of calculation of thermodynamic properties of mixtures including propane, butane and iso-butane we have selected the TRWW thermodynamic model with new constants published by Miyamoto and Watanabe (MW) [6-9] which covers a range of temperatures from the triple point temperature to 600 K, pressures up to 10 MPa. At the present stage the mentioned model is one of the most accurate models for calculation of equilibrium thermodynamic properties for propane in the gaseous and

liquid state. The absolute deviations of experimental thermodynamic property data from analytical model are mostly within ± 1%.

The relative deviation is defined by the following expression:

$$\text{Relative deviation} = \text{RD} = (\text{data}_{\text{LLL}} - \text{data}_{\text{TRWW}}) / \text{data}_{\text{TRWW}} \quad (19)$$

The results for all the models obtained by statistical thermodynamics show relatively good agreement. The computed vapour pressure, isothermal compressibility , molar isobaric heat capacity and speed of sound were confirmed well for all the models obtained by statistical thermodynamics. Somewhat larger deviations can be found in the region near the critical point due to the large influence of fluctuation theory and singular behaviour of some thermodynamic properties in the near-critical condition. The perturbation models on the basis of SAFT theory (LLL) yield surprisingly good results. The models on the basis of SAFT theory give better results in comparison with models on the basis of classical statistical thermodynamics, especially in high temperature and high pressure region.

Figures 1 and 2 show a comparison between LLL and TRWW models for speed of sound w, isothermal compressibility β and volumetric coefficient of expansion χ. The figures are elaborated for propane for the real gas phase at 5 MPa, 500 K and 0.1 MPa, 300 K in the dependence of molar fraction of butane. The largest deviations are 1.8% for speed of sound, 6% for volumetric coefficient of expansion and 3.1% for isothermal compressibility. The present analytical model yields very good results with much lower deviations in all other points.

Figure 3 shows a comparison between LLL and TRWW models for speed of sound, pressure, isobaric molar heat and isochoric molar heat for butane-propane mixture at 50% of molar fraction of butane at saturated gas conditions. The largest deviations are

1.8% for speed of sound w, 4.1% for pressure p, 4.1% for isochoric molar heat capacitc C_v and 13.1% for isobaric molar heat capacity C_p. The present analytical model yields very good results with much lower deviations in all other points.

Figure 4 shows a comparison between LLL and TRWW models for speed of sound w, pressure p, isobaric molar heat capacity C_p and isochoric molar heat capacity C_v for butane-iso-butane mixture at 50% of mole fraction of butane at saturated gas and saturated liquid conditions. The present analytical model yields very good results with much lower deviations in all other points.

The analysis shows that multi-pole effects must be taken into account for the areas of very low compressibility factors [31] to be able to expect full matching of results, even though the matching is even now very satisfactory. The present analysis provides a good basis for further upgrading of this model allowing the calculation of very accurate thermodynamic properties of state in liquid and gas phase as well as in super- and sub-critical region.

The results for all models obtained by statistical thermodynamics show relatively good agreement. The computed vapour pressure, isothermal compressibility , isobaric molar heat capacity and speed of sound have been well confirmed by our analytical model, obtained by statistical thermodynamics. Somewhat larger deviations can be found in the region near the critical point due to the significant influence of fluctuation theory and singular behaviour of some thermodynamic properties in the near-critical condition. The perturbation models on the basis of SAFT theory (LLL) yield surprisingly good results.

5. CONCLUSION AND SUMMARY

The paper presents the mathematical model for computation of thermodynamic functions of the state for hydrocarbons in the fluid state on the basis of statistical chain theory. The same procedure can be applied for calculation of therophysical properties for hydrofluorocarbons, of course with the knowledge of multipolar effects [20,31]. The analytical results are compared with the analytical calculation obtained by classical thermodynamics and show relatively good agreement.

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Table 2. The important constants for analytical calculation

	n-butane	*Iso*-butane	propane
σ_s (m)	3.87E-10	4.04E-10	3.77E-10
ε_s (J)	3.84E-21	3.219E-21	3.20E-21
M (-)	2.134	2.201	1.85

Figure captions

Fig. 1: Relative deviation of thermodynamic properties at 5 MPa

Fig. 2: Relative deviation of thermodynamic properties at 0.1 MPa

Fig. 3: Relative deviation of thermodynamic properties at saturated conditions for 50% of iso-butane and 50% of butane

Fig. 4: Relative deviation of thermodynamic properties at saturated conditions for 50% of *iso*-butane and 50% of butane

FIGURES

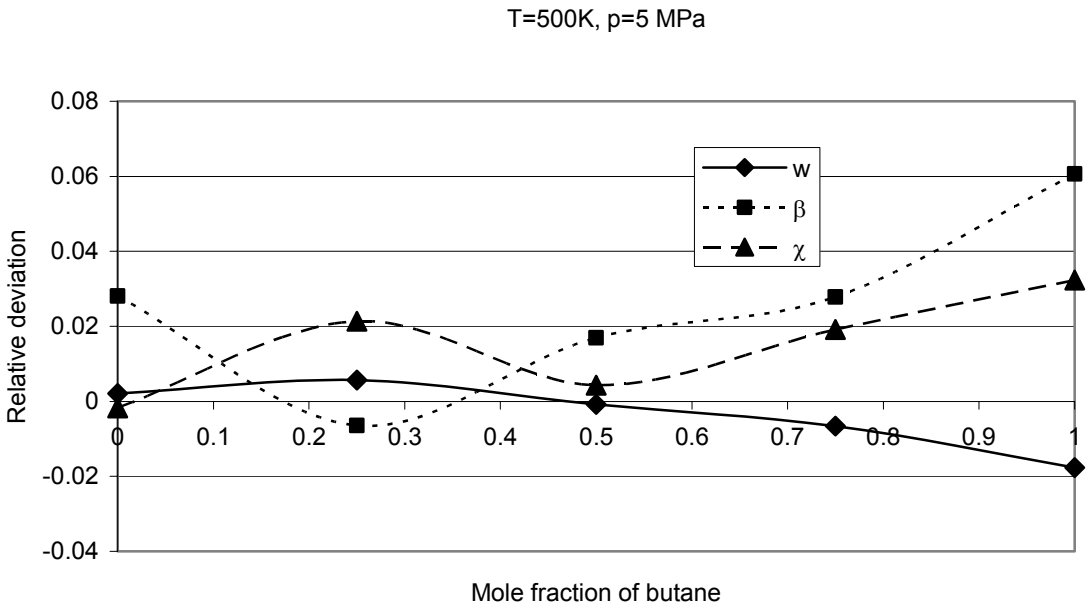

Fig. 1: Relative deviation of thermodynamic properties at 5MPa

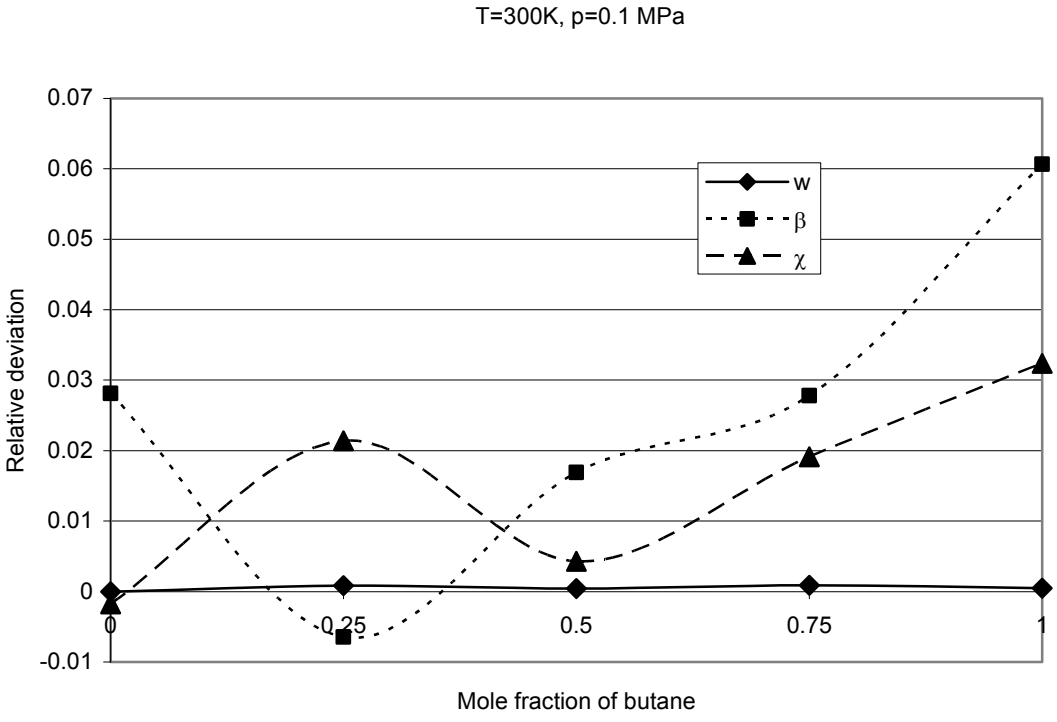

Fig. 2: Relative deviation of thermodynamic properties at 0.1 MPa

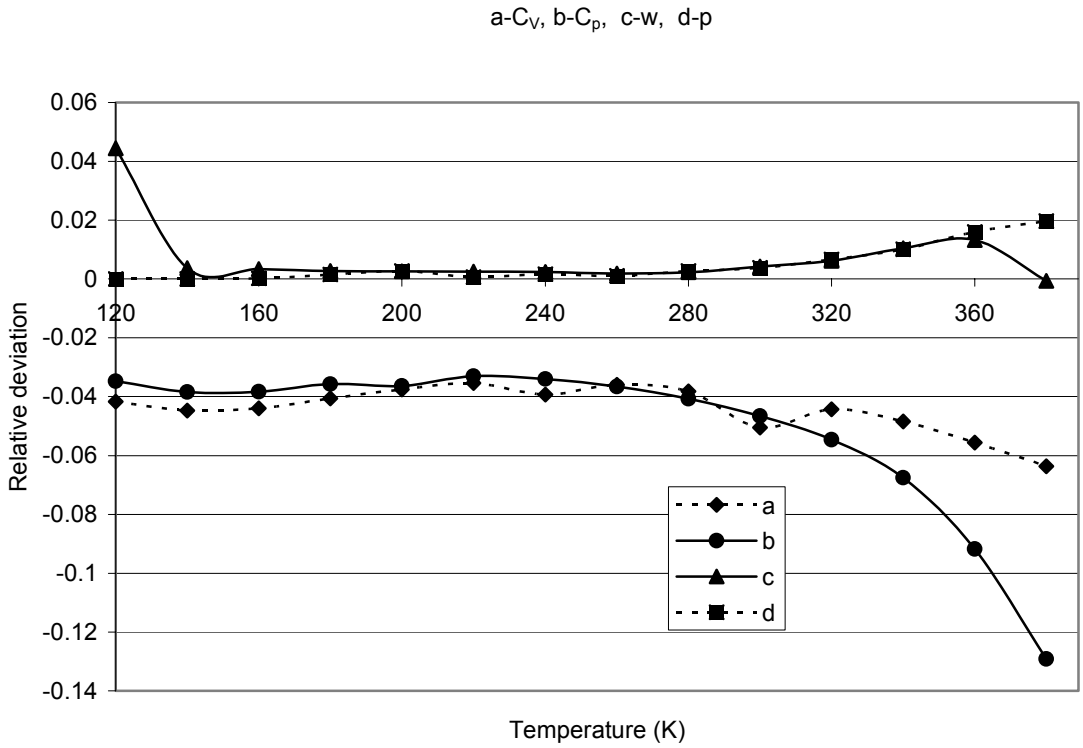

Fig. 3: Relative deviation of thermodynamic properties at saturated conditions for 50% of propane and 50% of n-butane

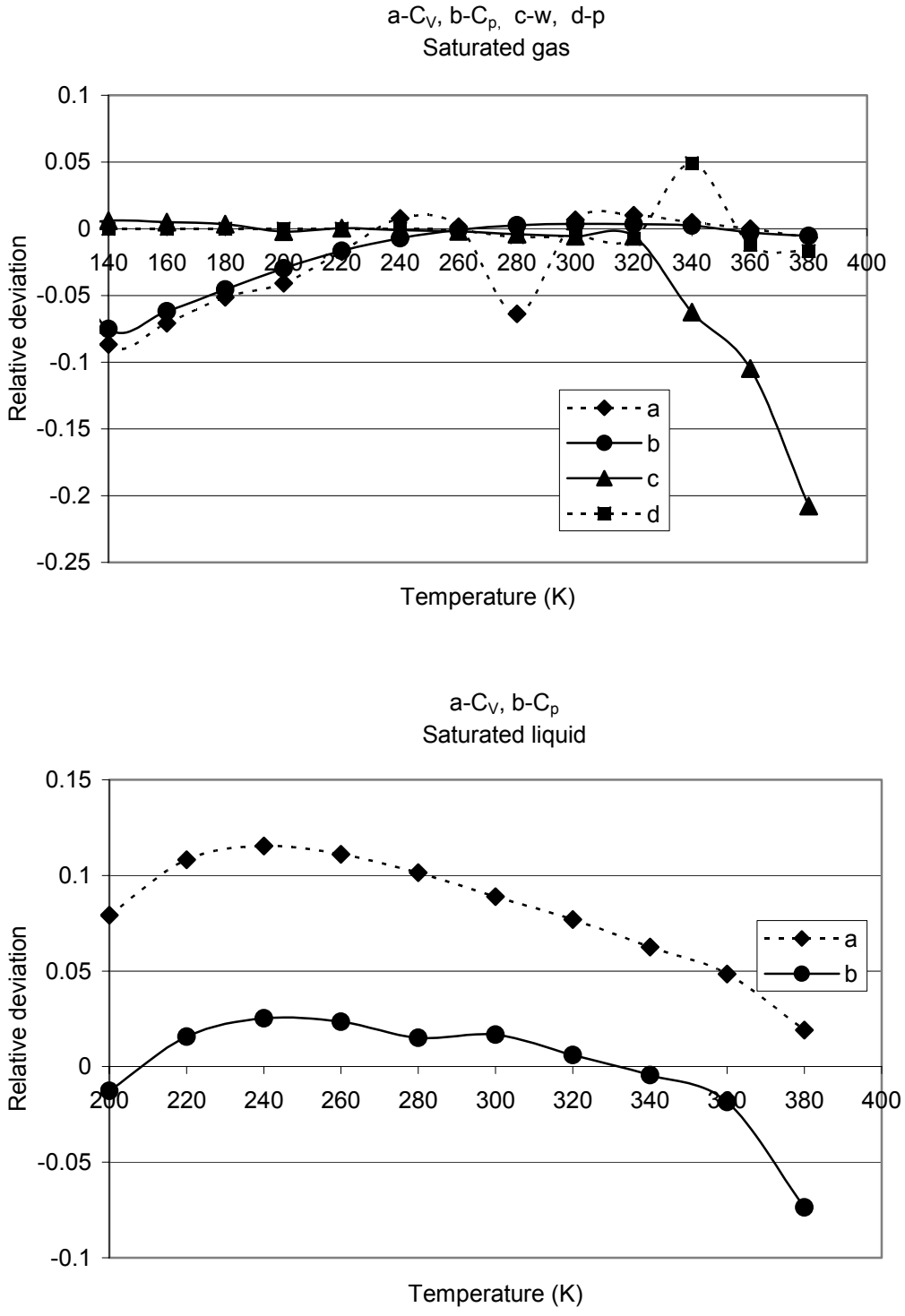

Fig. 4: Relative deviation of thermodynamic properties at saturated conditions for 50% of iso-butane and 50% of n-butane